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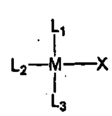


(I).

(57) **Abstract:** The present invention provides a complex of formula (I) wherein M is Ca, Mg, Ba or Sr, L_1 is selected from R^1O, R^2S, R^3R^4N, R^5R^6P, a substituted or unsubstituted cyclopentadienide, and a substituted or unsubstituted pyrazolyl group, where R^{1-6} are each independently H or hydrocarbyl; L_2 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7R^8C{=}NR^9$, $PR^7R^8R^9$, and a substituted or unsubstituted heterocycle containing one or more O, N or S atoms, Where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand; L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2, wherein L_3may be the same or different to L_2; or L_3 is linked to a further metal center ; or L_1, L_2 and L_3 are linked to form a tridentate ligand; and X is an alkyl group , an aryl group, an aryloxide, an amide group, or an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, wherein R^{10-12} are each independently H or hydrocarbyl; with the proviso that when L_1 and L_2 are $\{HC(C(CH_3){=}N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}$ and M is magnesium , X is other than Me or ^{t}Bu.

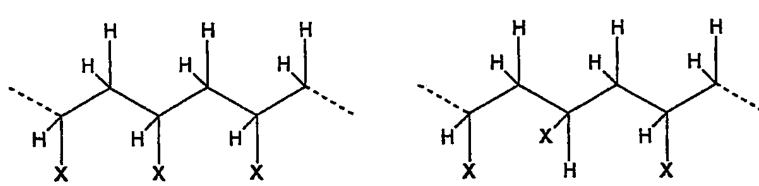
WO 03/062249 A2

COORDINATION COMPLEX

The present invention relates to a series of discrete, well-defined coordination complexes. More specifically, the invention concerns the use of Group 2 metal complexes in the controlled polymerisation of acrylate and alkylmethacrylate monomers.

Over recent years, an important technological objective has been the controlled, 'living' polymerisation of acrylate and alkylmethacrylate monomers to give products of controlled molecular weight and molecular weight distribution, and to provide access to block co-polymer materials. Examples of controlled or 'living' polymerisations include anionic polymerisation [C. Zune, R. Jérôme, Prog. Polym. Sci., 1999, 24, 631], group transfer polymerisation [O.W. Webster, W.R. Hertler, D.Y. Sogah, W.B. Farnham, T.V. Rajanbabu, J. Am. Chem. Soc., 1983, 105, 5706], atom transfer radical polymerisation [K. Matyjaszewski, J. Xia, Chem. Rev., 2001, 101, 2921], immortal polymerisation [T. Aida, S. Inoue, Acc. Chem. Res., 1996, 29, 39], catalytic chain transfer polymerisation [T.P. Davis, D.M. Haddleton, S.N. Richards, J. Macromol. Sci. Rev. Macromol. Chem. Phys., 1994, C34, 243], screened anionic polymerisation [D.G.H. Ballard, R.J. Bowles, D.M. Haddleton, S.N. Richards, R. Sellens, D.L. Twose, Macromolecules, 1992, 25, 5907] and metal-free anionic polymerisations [M.T. Reetz, Angew. Chem., Int. Ed. Engl. 1988, 27, 994].

Stereospecific polymers can exist in two different forms, isotactic and syndiotactic, as shown below.



ISOTACTIC SYNDIOTACTIC

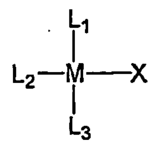
By way of contrast, an atactic polymer is one that has no regular arrangement along the chain.

Another important objective in the field of polymer chemistry has been to develop systems that can control the tacticity of products such as polymethylmethacrylate under industrially relevant process conditions. For example, the higher softening temperature accompanying highly syndiotactic polymethylmethacrylate confers beneficial properties on the resultant materials. Examples include s-PMMA for injection molding, artificial marble pre-mixes, stereocomplexes for preparing membranes and/or gel base materials, and syndiotactic-isotactic block PMMA for forming resist patterns.

To date, a number of systems have been described that can effect syndiotactic control in polymethylmethacrylate. These include organolanthanides [H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake and A. Nakamura, J. Am. Chem. Soc., 1992, 114, 4908; M. Nodono, T. Tokimitsu, S. Tone, T. Makino and A. Yanogase, Macromol. Chem. Phys., 2000, 201, 2282], zirconocenes [A.D. Bolig and E. Y.-X. Chen, J. Am. Chem. Soc., 2001, 123, 7943] aluminium compounds [T. Kitayama, T. Shinozaki, T. Sakamoto, M. Yamamoto and K. Hatada, Makromol. Chem. Suppl., 1989, 15, 167; G.L.N. Péron, R.J. Peace and A.J. Holmes, J. Mater. Chem., 2001, 11, 2915], magnesium compounds [T.Kitayama, T.Shinozaki, E. Masuda, M. Yamamoto and K. Hatada, Polym. Bull., 1988, 20, 565] and enamine initiators [M. Miyamoto and S. Kanetaka, J. Polym. Sci.: Part A: Polym. Chem., 1999, 37, 3671]. Most of these systems are accompanied by one or more limitations: either exceptionally low temperatures (e.g. –78°C or below) are required to obtain high syndiotacticity, and/or the molecular weight control over the resultant product is poor.

The present invention thus seeks to provide a series of discrete, well-defined coordination complexes that are useful as initiators in the polymerisation of alkylacrylate and/or alkylmethacrylate monomers. More specifically, the invention seeks to provide coordination complexes that are capable of influencing and/or controlling the syndiotacticity of the resulting polymer but which alleviate some of the above-mentioned problems associated with prior art complexes.

In a first aspect, the invention provides a complex of formula I



I

wherein

M is Ca, Mg, Ba or Sr;

L_1 is selected from R^1O, R^2S, R^3R^4N, R^5R^6P, a substituted or unsubstituted cyclopentadienide, and a substituted or unsubstituted pyrazolyl group, where R^{1-6} are each independently H or hydrocarbyl;

L_2 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7R^8C{=}NR^9$, $PR^7R^8R^9$, and a substituted or unsubstituted heterocycle containing one or more O, N or S atoms, where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand;

L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2, wherein L_3 may be the same or different to L_2; or L_3 is linked to a further metal centre; or L_1, L_2 and L_3 are linked to form a tridentate ligand; and

X is an alkyl group, an aryl group, an amide group, an aryloxide or an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, wherein R^{10-12} are each independently H or hydrocarbyl;

with the proviso that when L_1 and L_2 are $\{HC(C(CH_3){=}N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}$ and M is magnesium, X is other than Me or ${}^tBu$.

In a first aspect, the present invention therefore relates to a complex wherein L_1 is a monoanionic ligand, and L_2 and L_3, if present, are both neutral ligands.

Thus, where L_1 is a substituted or unsubstituted cyclopentadienide, this refers to a monoanionic substituted or unsubstituted cyclopentadiene nucleus which complexes to the metal M. Likewise, where L_1 is a substituted or unsubstituted pyrazolyl group, this refers to a monoanionic pyrazole nucleus. Preferably, the monoanionic pyrazole nucleus complexes to the metal, M, through one of the nitrogen atoms.

As used herein, the term "hydrocarbyl" refers to a group comprising at least C and H that may optionally comprise one or more other suitable substituents. Examples of such substituents may include halo-, alkoxy-, nitro-, an alkyl group, or a cyclic group. In addition to the possibility of the substituents being a cyclic group, a combination of substituents may form a cyclic group. If the hydrocarbyl group comprises more than one C then those carbons need not necessarily be linked to each other. For example, at least two of the carbons may be linked via a suitable element or group. Thus, the hydrocarbyl group may contain heteroatoms. Suitable heteroatoms will be apparent to those skilled in the art and include, for instance, sulphur, nitrogen, oxygen, phosphorus and silicon.

Preferably, M is Ca or Mg.

In a preferred embodiment, R^1 and R^2 are each independently hydrocarbyl, and R^{3-6} are each independently H or hydrocarbyl.

In a particularly preferred embodiment, R^1 and R^2 are each independently selected from branched or unbranched alkyl, branched or unbranched alkenyl, or aryl, each of which may be substituted or unsubstituted. Suitable substituents include, for example, alkyl, halo-, alkoxy-, nitro-, or a cyclic group.

As used herein, the term "alkyl" refers to a saturated carbon-containing chain which may be straight or branched, and substituted (mono- or poly-) or unsubstituted. Suitable substituents include those which do not have any significant adverse effect on the activity of the complex and may include, for example, halo-, alkoxy-, nitro-, or a cyclic group.

Preferably, the alkyl group is a C_{1-20} alkyl group, more preferably a C_{1-10} alkyl group.

Accordingly, the term "haloalkyl" refers to an alkyl group substituted by at least one halogen, for example, chlorine, bromine, fluorine or iodine.

Accordingly, the term "heteroalkyl" refers to an alkyl group containing at least one heteroatom, for example, O, N or S.

As used herein, the term "alkenyl" refers to a C_{2-20} unsaturated carbon-containing chain which may be branched or unbranched, and substituted (mono- or poly-) or unsubstituted. Preferably the alkenyl group is a C_{2-10} alkenyl group.

As used herein, the term "aryl" refers to a C_{6-10} aromatic, substituted (mono- or poly-) or unsubstituted. Again, suitable substituents include those which do not have any significant adverse effect on the activity of the complex and may include, for example, alkyl, halo-, alkoxy-, nitro-, or a cyclic group.

As used herein, the term "cycloalkyl" refers to a cyclic alkyl group which may be substituted (mono- or poly-) or unsubstituted.

As used herein, the term "heterocycle" refers to an aromatic or non-aromatic heterocycle comprising one or more heteroatoms. Preferred heterocycle groups include pyrrole, pyrazole, pyrimidine, pyrazine, pyridine, quinoline, thiophene and furan.

In one preferred embodiment, X is an alkyl group. In an especially preferred embodiment, X is ^{i}Pr.

In another preferred embodiment, X is an amide group. Even more preferably, X is NPr^{i}_{2}.

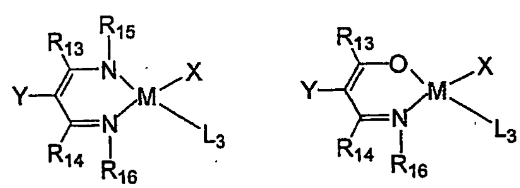
In another preferred embodiment, X is an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, wherein R^{10-12} are each independently H or hydrocarbyl. Preferably, R^{10} and R^{11} are H and R^{12} is an aryl group.

In one particularly preferred embodiment, X is -OC (=CH_2)Ar, wherein Ar = 2,4,6,-$Me_3C_6H_2$.

In one preferred embodiment, L_3 is THF or Et_2O.

In another preferred embodiment, L_1 and L_2 are linked to form a bidentate ligand selected from derivatives of acetylacetonate, e.g. a beta-diketiminate or a beta-ketoiminate.

In one preferred embodiment, the complex of the invention is of formula II or III



II III

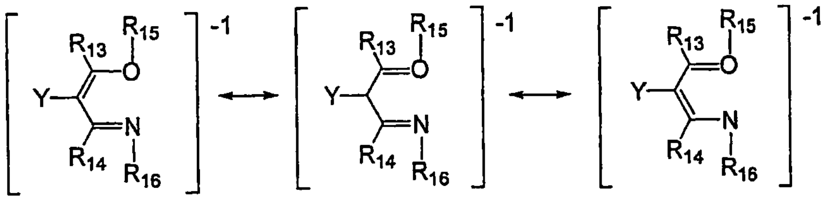
wherein

Y is H, halogen, NO_2, hydrocarbyl or CN;

R^{13-16} are each independently selected from H and hydrocarbyl; or Y and R^{13} are linked to form a hydrocarbyl group; and

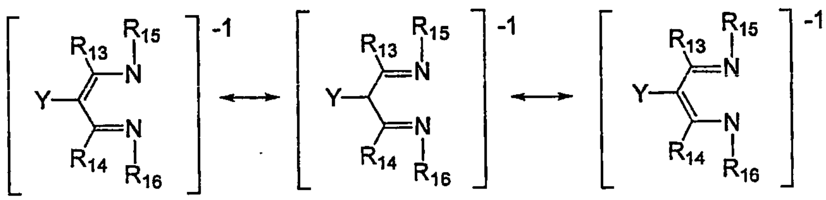
L_3 is as defined above.

The skilled person will appreciate that ligands of formula III will have an overall charge of –1 and may exist in one or more of the isomeric forms shown below, or mixtures thereof, or a hybrid thereof in which the electrons are delocalised throughout the whole ligand system.



IIIa IIIb IIIc

Likewise, the skilled person will appreciate that ligands of formula II will have an overall charge of −1 and may exist in one or more of the isomeric forms shown below, or mixtures thereof, or a hybrid thereof in which the electrons are delocalised throughout the whole ligand system.



IIa IIb IIc

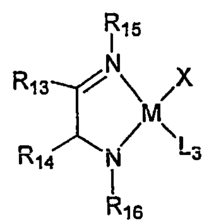
As used herein, and throughout the accompanying claims and Examples, the shorthand representation of the di-imine isomer IIb, {YC(C(R')=N-R'')$_2$}, is used for simplicity to represent all of the above isomeric forms of ligand II, in the case where R^{13} and R^{14} are the same (represented as R') and R^{15} and R^{16} are the same (represented as R'').

In a more preferred embodiment, where the complex of the invention is of formula II or III, Y is selected from H, halogen, NO_2, CN, alkyl, aryl, haloalkyl or heteroalkyl;
R^{13-16} are each independently selected from alkyl, aryl, heteroalkyl, haloalkyl, cycloalkyl and a heterocyclic ring containing at least one O, N or S atom; or Y and R^{13} are linked to form an aryl group; and
L_3 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7C{=}NR^8$, $PR^7R^8R^9$, thiophene and tetrahydrofuran, where R^{7-9} are each independently H or a hydrocarbyl group.

Preferably, where the complex of the invention is of formula II or III, R^{13} and R^{14} are each independently alkyl. In one especially preferred embodiment, R^{13} and R^{14} are the same. More preferably still, R^{13} and R^{14} are both methyl or are both ^{t}Bu.

Preferably, where the complex of the invention is of formula II or III, R^{15} and R^{16} are each substituted aryl groups. In one especially preferred embodiment, R^{15} and R^{16} are the same. More preferably still, R^{15} and R^{16} are both 2,6-diisopropylphenyl.

In another preferred embodiment, the complex of the invention is of formula V



V

wherein $R^{13\text{-}16}$ are as defined above, and where R^{13} and R^{15} are optionally linked to form an aryl group.

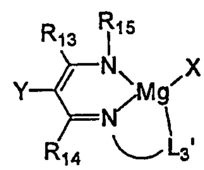
Preferably, where the complex of the invention is of formula V, R^{13} and R^{14} are the same.

Preferably, where the complex of the invention is of formula V, R^{15} and R^{16} are the same.

In one preferred embodiment of the invention, L_1, L_2 and L_3 are linked to form a tridentate ligand.

In a particularly preferred embodiment, L_1, L_2 and L_3 are linked to form a tridentate ligand selected from a beta-diketiminate with a pendant donor group, a Schiff base derivative with a pendant donor arm, and a tris(pyrazolyl)borate ligand.

Even more preferably, the complex of the invention is of formula



VI

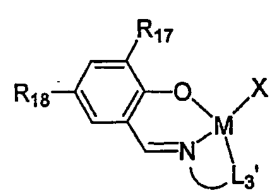
wherein L_3' is defined as for L_3 above, and is linked to the nitrogen of the bidentate ligand via a linker group.

More preferably, the linker group is an aryl group.

In one particularly preferred embodiment, $L_{3'}$ is an alkoxy group. Even more preferably, the alkoxy group $L_{3'}$ is attached to an aryl linker group.

In the case where the complex is of formula VI, preferably Y is H, R^{13} and R^{14} are both methyl, R^{15} is aryl (preferably 2,6-diisopropylphenyl) and X is isopropyl.

In an alternative preferred embodiment, the complex of the invention is of formula VII

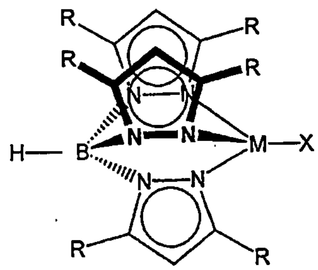


VII

wherein L_3' is defined as for L_3 above, and is linked to the nitrogen of the bidentate ligand via a linker group, and R^{17-18} are as defined for R^{13-16} above .

Preferably, where the complex is of formula VI or VII, the linker group is $(CH_2)_n$ where n is 0-6, an arylene group, or SiR_2, where R is a hydrocarbyl group.

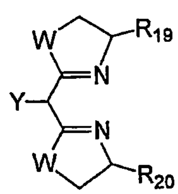
In another preferred embodiment of the invention, L_1, L_2 and L_3 are linked to form a tris(pyrazolyl)borate ligand which complexes to metal M as shown below, where each R is independently H or a hydrocarbyl group.



X

The tris(pyrazolyl)borate ligand has an overall charge of −1, i.e., one of the pyrazolyl groups bonds to the metal M as a monoanionic ligand (L_1), whereas the remaining two pyrazolyl groups (L_2, L_3) complex to metal M as neutral ligands. However, the skilled artisan will appreciate that the electrons in the above tris(pyrazolyl)borate complex are delocalised throughout the whole system.

In yet another preferred embodiment of the invention, L_1 and L_2 form a bidentate ligand of formula VIII



VIII

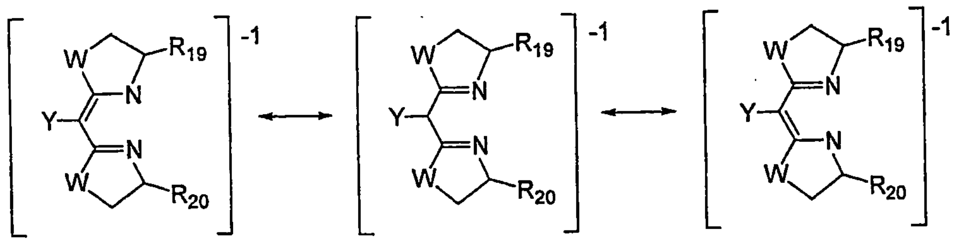
wherein

Y is as defined above;

W is O, NH, NR''' or CH_2, where R''' is a hydrocarbyl group; and

R^{19-20} are as defined for R^{13-16} above.

The skilled person will appreciate that the ligand of formula VIII will have an overall charge of –1 and may exist in one or more of the isomeric forms shown below, or mixtures thereof.



In one preferred embodiment, the invention comprises a dimer of a complex as described hereinbefore, or higher nuclearity aggregates.

In an especially preferred embodiment, the complex of the invention is selected from the following:

$\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg{}^iPr$ **[1]**;

$[\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)]_2$ **[2]**;

$[\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg(OC(=CH2)Ar)\cdot Et_2O]$ **[3]**;

wherein $Ar = 2,4,6,\text{-}Me_3C_6H_2$;

$\{HC(C({}^tBu)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)\text{-}2,4,6\text{-}Me_3C_6H_2)$ **[4]**;

$\{HC(C(Me)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)(C(Me)=N\text{-}2\text{-}OMeC_6H_4)\}Mg{}^iPr$ **[5]**;

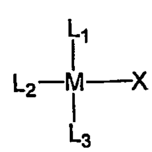
$\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Mg(OC(=CH_2)\text{-}2,4,6\text{-}Me_3C_6H_2)$ **[6]**;

$\{HC(C(Me)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Ca(OC(=CH_2)\text{-}2,4,6\text{-}Me_3C_6H_2)\cdot THF$ **[7]**;

$[\{HC(C(Me)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Ca(OC(=CH_2)\text{-}2,4,6\text{-}Me_3C_6H_2)]_n$ **[8]** where n = 1 or 2; and

$\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}MgNPr^i_2$ **[9]**.

In a second aspect, the invention relates to the use of a complex of formula Ia as a polymerisation initiator,



Ia

wherein

M is Ca, Mg, Ba or Sr;

L_1 is selected from R^1O, R^2S, R^3R^4N, R^5R^6P, a substituted or unsubstituted cyclopentadienide, and a substituted or unsubstituted pyrazolyl group, where R^{1-6} are each independently H or hydrocarbyl;

L_2 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7R^8C{=}NR^9$, $PR^7R^8R^9$, and a substituted or unsubstituted heterocycle containing one or more O, N or S atoms, where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand;

L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2, wherein L_3 may be the same or different to L_2; or L_3 is linked to a further metal centre; or L_1, L_2 and L_3 are linked to form a tridentate ligand; and

X is an alkyl group, an aryl group, an amide group, or an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, wherein R^{10-12} are each independently H or hydrocarbyl;

with the proviso that when L_1 and L_2 are $\{HC(C(CH_3){=}N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}$, M is magnesium, X is other than Me or ^tBu.

Preferably, M is Ca or Mg.

The preferred embodiments for the second aspect of the invention are identical to those described hereinabove for the first aspect.

In a preferred embodiment, the invention relates to the use of a complex of formula Ia in the polymerisation of acrylate and/or alkylacrylate monomers. In particular, the complexes of the present invention are capable of influencing the tacticity of the resulting polymer. More specifically, the complexes of the invention are capable of inducing a high degree of syndiotacticity in the resulting polymer.

As used herein, the term "acrylate monomer" refers to an acrylate monomer which is optionally substituted by one or more hydrocarbyl groups as defined hereinabove.

Similarly, the term "alkylacrylate monomer" refers to an alkylacrylate monomer which is optionally substituted by one or more hydrocarbyl groups as defined hereinabove.

Preferably, said acrylate and alkylacrylate monomers are substituted by branched acyclic and cyclic hydrocarbons and/or functionalised substituents such as hydroxyalkyl, glycidyl and glycolethers.

In one preferred embodiment, the acrylate monomer is an alkylacrylate.

In another preferred embodiment, the alkylacrylate monomer is an alkylmethacrylate.

One preferred embodiment relates to the use of complexes in accordance with the second aspect of the invention as initiators in the preparation of block copolymers. By way of example, said complexes may be used in the preparation of a block copolymer of methyl methacrylate and n-butyl methacrylate. Further details of this aspect of the invention are provided in the accompanying examples section.

In a third aspect, the invention provides a process for the polymerisation of acrylate and/or alkylacrylate monomers, said process comprising contacting an initiating amount of a complex of formula Ia as defined above with an acrylate and/or an alkylacrylate monomer in the presence of a suitable solvent.

In a preferred embodiment, the invention provides a polymerisation process for preparing a block copolymer, for example, a block copolymer of methyl methacrylate and n-butyl methacrylate.

In a further preferred aspect, the polymerisation takes place in the presence of a chain transfer reagent.

Preferably, the chain transfer reagents have an acidic proton in the alpha position to a carbonyl group and are of the formula Z-CH_2-C(=O)-R", wherein R" is H, alkyl or aryl, and Z is selected from aryl, alkyl, H, amino, alkylamino, acyl, alkoxy (OR), thiol (SR) or heterocycle, where R is a hydrocarbyl group.

An example of a chain transfer reagent in which Z is aryl is 2',4',6'-trimethylacetophenone. Examples of chain transfer reagents in which Z is alkylamino include amino methyl ketones and amino ethyl ketones. An example of a chain transfer reagent in which Z is acyl is 2,4-pentanedione, i.e. Z is C(=O)CH_3 and R" is CH_3.

Other suitable chain transfer reagents are known in the literature and will be apparent to the person skilled in the relevant art.

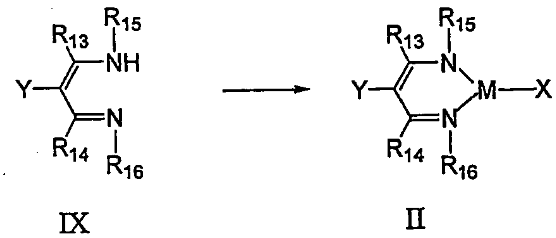
Preferably, the ratio of monomer to the complex in the above process is between 10:1 to 10^6:1.

A fourth aspect of the invention provides an article prepared by the above-described process.

A fifth aspect of the invention provides a composition comprising an acrylate and/or an alkylacrylate monomer and a complex of formula Ia as defined above.

A sixth aspect of the invention provides a composition comprising poly(alkylacrylate) and/or poly(alkylmethacrylate) or co-polymers thereof, and a complex of formula Ia as defined above.

A seventh aspect of the invention relates to a process for preparing a complex of formula II as defined hereinabove, where X is alkyl, said process comprising reacting a compound of formula IX with (a) ^{n}BuLi, and (b) XMgCl



Alternatively, in an eighth aspect of the invention, the complex of formula II may be prepared by reacting a compound of formula IX with a di(alkyl)magnesium compound, MgX_2.

In a ninth aspect, the invention provides a process for preparing a complex of formula II, as defined above, where X is an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, said process comprising reacting the product obtained from the above-described seventh and eighth aspects with a compound of formula $HR^{10}R^{11}C\text{-}C(O)R^{12}$.

A tenth aspect of the invention provides a method for producing poly(alkylacrylate) or poly(alkylmethacrylate) having a syndiotacticity of greater than 75%, and preferably greater than 85%, said method comprising contacting the corresponding monomer (alkyl acrylate, or alkylmethacrylate, or mixtures thereof) with a complex of formula Ia as defined above in a suitable solvent.

Preferably, said method is carried out at a temperature in excess of -40°C.

Thus, in one particularly preferred embodiment, the complex of the invention is capable of affording polymethylmethacrylate with greater than 90% syndiotacticity in a highly controlled manner at a temperature in excess of -40°C.

The invention is further described by way of example and with reference to the following figures wherein:

Figure 1 shows the X-ray crystal structure for the compound [{HC(C(CH_3)=N-2,6-$^iPr_2C_6H_3)_2$}Mg(OC(=CH_2)Ar)]$_2$.

Figure 2 shows a graph to illustrate the relationship between monomer conversion and M_n as determined by GPC (polydispersities, M_w/M_n, quoted in brackets).

EXAMPLES

Example 1

Synthesis of {HC(C(CH_3)=N-2,6-$^iPr_2C_6H_3)_2$}Mg^{i}Pr **[1]**

$H_2C(C(CH_3)$=N-2,6-$^iPr_2C_6H_3)_2$ (6.880g, 1.64 x 10^{-2}mol) was dissolved in 50cm^3 toluene and lithiated via the addition of 6.7cm^3 ^{n}BuLi (2.5M in hexane, 1.68 x 10^{-2}mol). In a separate vessel 8.4cm^3 ^{i}PrMgCl (2.0M in Et_2O, 1.68 x 10^{-2}mol) was diluted with 10cm^3 toluene and concentrated under reduced pressure to a white viscous liquid. This procedure was repeated in order to remove most of the Et_2O from the Grignard reagent to avoid formation of [{HC(C(CH_3)=N-2,6-$^iPr_2C_6H_3)_2$}Mg^{i}Pr•Et_2O]. The white sticky oil thus obtained was suspended in 20cm^3 toluene and this mixture was then added dropwise to the solution of {HC(C(CH_3)=N-2,6-$^iPr_2C_6H_3)_2$}Li to afford a pale yellow, cloudy suspension.

The reaction was stirred overnight (18hours) at room temperature and then filtered. Volatiles were removed in vacuo and the resultant cream coloured solid was washed with 5cm^3 cold (-78°C) n-pentane to afford 7.732g of a slightly off-white powder (1.59 x 10^{-2}mol, 97.0%).

^{1}H NMR (C_6D_6): δ 7.10 (m, 6H, *m-H, p-H*), 4.92 (s, 1H, *H*C{C(CH_3)NAr}$_2$), 3.13 (sept, 4H, $^3J_{HH}$ = 6.9Hz, C*H*Me$_2$), 1.67 (s, 6H, HC{C(C*H*$_3$)NAr}$_2$), 1.26 (d, 12H, $^3J_{HH}$ = 6.9Hz, CH(C*H*$_3$)$_2$), 1.14 (d, 12H, $^3J_{HH}$ = 6.9Hz, CH(C*H*$_3$)$_2$), 0.86 (d, 6H, $^3J_{HH}$ = 6.6Hz, MgCH(C*H*$_3$)$_2$), 0.13 (sept, 1H, $^3J_{HH}$ = 6.3Hz, MgC*H*(CH_3)$_2$). ^{13}C NMR (C_6D_6): δ 168.84 (HC{*C*(CH_3)NAr}$_2$), 143.63 (C_{ipso}), 141.41 (C_{ortho}), 125.71 (C_{para}), 123.80 (C_{meta}), 94.89 (*H*C{C(CH_3)NAr}$_2$), 28.39 (ArCH(CH_3)$_2$), 24.10 (HC{C(CH_3)NAr}$_2$),

24.02 ($MgCH(CH_3)_2$), 23.15 ($ArCH(CH_3)_2$), 9.22 ($MgCH(CH_3)_2$). Elemental analysis for $C_{32}H_{48}N_2Mg$: C 79.24, H 9.97, N 5.78%. Found C 79.31, H 9.94, N 5.68%.

Example 2

Synthesis of $[\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)]_2$ (Ar = 2,4,6,-$Me_3C_6H_2$) **[2]**

0.8240g $\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg^iPr$ (1.70×10^{-3}mol) was suspended in 20cm^3 toluene in a Schlenk tube placed in a solid CO_2 / acetone slush bath at -78°C. A 5cm^3 toluene solution of 2',4',6'-trimethylacetophenone (0.2756g, 1.70×10^{-3}mol), also at -78°C, was then added dropwise over 5 minutes to afford a dark orange solution. On warming to ambient temperature the solution becomes increasingly pale yellow.

The reaction was stirred at room temperature for 18 hours. Removal of volatiles from the pale yellow-green solution gave a white solid which was then washed with 10cm^3 cold heptane (-78°C). A saturated solution was then prepared by stirring the residual white powder in 15cm^3 heptane at 60°C for 30 minutes. The solution was filtered and allowed to slowly cool to yield very pale yellow rhomboid crystals of X-ray diffraction quality.

A second crop was prepared by reducing the volume of the mother liquor to approximately two-thirds and storing overnight in a freezer at -10°C.
Total yield: 0.673g, 5.58×10^{-4}mol, 65.7%

Example 3

Synthesis of $[\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg(OC(=CH2)Ar)\bullet Et_2O]$ (Ar = 2,4,6,-$Me_3C_6H_2$) **[3]**

A chilled (-78°C) 10cm^3 Et_2O solution of 2',4',6'-trimethylacetophenone (0.4156g, 2.56 x 10^{-3}mol) was added dropwise over 30 minutes to a 10cm^3 Et_2O solution of $\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg^iPr$ (1.2315g, 2.54×10^{-3}mol) in a solid CO_2 / acetone slush bath at -78°C. The reaction was allowed to warm to room temperature to give a pale yellow coloured solution, which was then stirred for a further 18 hours. Volatiles were removed *in vacuo* to give a sticky, cream-coloured solid which was

washed with $5cm^3$ pentane at -78°C to yield 1.312g of a white powder (1.94×10^{-3}mol, 76.3%).

Example 4

Typical polymerisation procedure for $[\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)]_2$ [2]

0.0084g $[\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)]_2$ (1.39×10^{-5}mol) was weighed out into a glass vial and dissolved in $5cm^3$ toluene to afford a pale yellow solution. The solution was cooled to –30°C. Methyl methacrylate (0.4183g, 4.18×10^{-3}mol, 300 equivalents) was then weighed out and cooled to –30°C and added to the initiator solution. The mixture was stirred for 10 minutes, followed by termination of the polymerisation by addition of 25μl MeOH.

GPC analysis was performed on a small aliquot, which was removed and dried in vacuo. The remainder of the solution was added to a large excess (ca. $150cm^3$) MeOH, and the precipitate was collected and dried. ^1H NMR analysis ($CDCl_3$) gave 92% rr, 8%rm, (mm triad undetected).

Example 5

Typical polymerisation procedure for $[\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)\cdot Et_2O]_2$ [3]

An identical method to that described above was employed. No significant differences in the behaviour of the polymerisation using the etherate initiator were observed.

Example 6

Typical polymerisation procedure for $[\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg{}^iPr]$ [1]

An identical method to the procedure outlined for $[\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)]_2$ was used. Immediately upon addition of methyl methacrylate to the initiator solution a bright yellow colouration was observed, which quickly became pale yellow. This colour persisted through the remainder of the reaction, disappearing upon addition of MeOH.

Example 7

Investigation into the relationship between conversion and molecular weight

Using a similar method to that described above, 0.0080g [{HC(C(CH_3)=N-2,6-$^iPr_2C_6H_3$)$_2$}Mg(OC(=CH_2)Ar)]$_2$ (1.33 x 10^{-5}mol) was dissolved in 6cm^3 $CDCl_3$. To this solution at -30°C was added neat methyl methacrylate (0.5317g, 5.31 x 10-3mol, 400 equivalents). The reaction was stirred at -30°C and at set time periods (120, 240, 360 and 480 seconds), 0.35cm^3 aliquots were removed and immediately terminated by addition to 20μl MeOH.

Monomer conversion was calculated by diluting the samples with a further 0.35cm^3 $CDCl_3$ and integrating the ^{1}H NMR resonances of the OCH_3 signals of the monomer (δ3.71) versus the polymer (δ3.56). Volatiles were then removed in vacuo and the residue was dissolved in non-deuterated $CHCl_3$. Analysis of this solution by gel permeation chromatography afforded a correlation of M_n versus conversion (see Figure 2).

Example 8

Block copolymerisation of n-butylmethacrylate (BMA) and methylmethacrylate (MMA)

0.0106g [{HC(C(CH_3)=N-2,6-$^iPr_2C_6H_3$)$_2$}Mg(OC(=CH_2)Ar)]$_2$ (1.76 x 10^{-5}mol) was dissolved in 3cm^3 $CDCl_3$ at -30°C. To this stirring solution was added 0.2526g BMA (1.78 x 10^{-5}mol, 101 equivalents). After 10 minutes a 300μl aliquot was removed and terminated by addition to 10μl MeOH. The polymerisation was allowed to stir for a further 60 seconds and then 0.1756g MMA (1.75 x 10^{-5}mol, 100 equivalents) was added. The reaction was stirred for a further 10 minutes and terminated by addition of 25μl MeOH. ^{1}H NMR on the aliquot revealed that before the addition of the second monomer the BMA had been totally consumed.

GPC on the aliquot before addition of the MMA showed a single, monodisperse peak (Mn calc = 14,400, Mn obs = 13,800, Mw/Mn = 1.12). GPC on the block copolymer demonstrated Mn increased upon the incorporation of the MMA (Mn calc = 24,400, Mn obs = 22,800, Mw/Mn = 1.50).

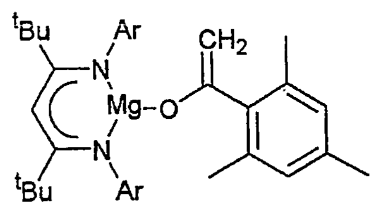
Example 9

The use of 2',4',6'-trimethylacetophenone as a chain transfer agent

To a $3cm^3$ $CDCl_3$ solution of $[\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)Ar)]_2$ (0.0130g, 2.16×10^{-5}mol) at -30°C was added 17.9µl 2',4',6'-trimethylacetophenone (1.08×10^{-4}mol, 5.0 equivalents) to afford a bright yellow solution. 0.8675g MMA (8.66×10^{-5}mol, 402 equivalents) was then added. After 30 minutes the reaction was terminated by the addition of 25µl MeOH. GPC Mn calc (assuming maximum chain transfer) = 6,700; Mn obs = 7,200, Mw/Mn = 2.83).

Example 10

Synthesis of $\{HC(C({}^tBu)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)\text{-}2,4,6\text{-}Me_3C_6H_2)$ **[4]**



Ar = 2,6-$^iPr_2C_6H_3$

0.8902g $H_2C(C({}^tBu)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2$ (1.77×10^{-3}mol) was dissolved in $10cm^3$ toluene and then chilled to -78°C. Bu_2Mg ($1.86cm^3$, 1.0M solution in heptane, 1.86×10^{-3}mol, 1.05 equivalents) was added dropwise over 5 minutes, and upon removal from the cold bath a light yellow solution developed. The reaction was allowed to reach room temperature and then stirred for 2 hours at 60°C. The reaction vessel was then allowed to cool to room temperature before $0.30cm^3$ 2',4',6'-trimethylacetophenone (1.81×10^{-3}mol, 1.02 equivalents) was added. The mixture was then warmed back to 60°C and stirred for 90 mins. The volatile components were then removed *in vacuo* to give a yellow oily solid which was washed with pentane ($5cm^3$) at -78°C.

^1H NMR (C_6D_6): δ 7.12-6.97 (m, 6H, N-2,6-$^iPr_2C_6H_3$), 6.72 (s, 2H, 2,4,6-$Me_3C_6H_2$), 5.40 (s, 1H, $HC\{C({}^tBu)=NAr\}_2$), 3.77 (d, $^2J_{HH}$ = 0.9Hz, 1H, OC(=C*H*H)Ar'), 3.66 (d, $^2J_{HH}$ = 1.0Hz, 1H, OC(=CH*H*)Ar'), 3.22 (sept, 4H, $^3J_{HH}$ = 6.9Hz, C*H*MeMe) 2.17 (s,

6H, mesityl *o-CH₃*), 1.98 (s, 3H, mesityl *p-CH₃*), 1.22 (d, 12H, $^3J_{HH}$ = 6.8Hz, CH*Me*Me), 1.21 (d, 12H, $^3J_{HH}$ = 6.98Hz, CH*Me*Me), 1.14 (s, 18H, HC{C(C*Me₃*)=NAr}₂).

Example 11

Use of {HC(C(^{t}Bu)=N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$}Mg(OC(=CH$_2$)-2,4,6-Me$_3$C$_6$H$_2$) [4] as an MMA polymerisation initiator

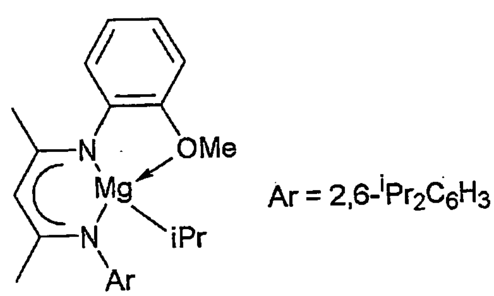
A similar method to that described for the synthesis of {HC(C(Me)=N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$}Mg(OC(=CH$_2$)-2,4,6-Me$_3$C$_6$H$_2$) was used. The polymerisation using {HC(C(^{t}Bu)=N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$}Mg(OC(=CH$_2$)-2,4,6-Me$_3$C$_6$H$_2$) is slower, however. Thus, for 200 equivalents MMA a reaction time of 120 minutes is required at -30°C to afford x% conversion (c.f. < 5 minutes for {HC(C(Me)=N-2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$}Mg(OC(=CH$_2$)-2,4,6-Me$_3$C$_6$H$_2$).

M_n = 17,100 (M_n calc = 20,000); M_w/M_n = 1.04.

Syndiotactic content (% rr triad) = 90%

Example 12

Synthesis of {HC(C(Me)=N-2,6-^{i}Pr$_2$C$_6$H$_3$)(C(Me)=N-2-OMeC$_6$H$_4$)}Mg^{i}Pr [5]



^{n}Butyl lithium (2.70 mL, 2.5M in hexanes, 6.75 x 10^{-3}mol) was added slowly to a stirred solution of {H$_2$C(C(Me)=N-2,6-^{i}Pr$_2$C$_6$H$_3$)(C(Me)=N-2-OMeC$_6$H$_4$)} (2.46 g, 6.75 x 10^{-3}mol) in 25 mL toluene at 0°C. The solution was stirred for 24 hours before addition of ^{i}PrMgCl (3.37cm^3, 2.0M in Et$_2$O, 6.74 x 10^{-3}mol) at 0°C. The solution was then stirred for a further 18 hours at ambient temperature. Concentration of the solution under reduced pressure afforded an orange solid (2.1 g, 4.98 x 10^{-3}mol, 73.9 %).

^1H NMR (C_6D_6): δ 6.87, 6.79, 6.48 (m, 7H, Ar*H*), 4.90 (s, 1H, *H*C{C(CH$_3$)NAr}$_2$), 3.32 (s, 3H, ArOC*H*$_3$), 3.20 (sept, 1H, $^3J_{HH}$ = 6.86 Hz, ArC*H*Me$_2$), 1.92 (s, 3H, HC{C(C*H*$_3$)NAr}$_2$), 1.68 (s, 3H, HC{C(C*H*$_3$)NAr}$_2$), 1.24 (d, 6H, $^3J_{HH}$ = 6.44 Hz, ArCH(C*H*$_3$)$_2$), 1.23 (d, 6H, $^3J_{HH}$ = 7.86 Hz, MgCH(C*H*$_3$)$_2$), 1.16 (d, 6H, $^3J_{HH}$ = 6.83 Hz, ArCH(C*H*$_3$)$_2$), 0.07 (sept, 1H, $^3J_{HH}$ = 7.83 Hz, MgC*H*Me$_2$).

Example 13

Use of {HC(C(Me)=N-2,6-^{i}Pr$_2$C$_6$H$_3$)(C(Me)=N-2-OMeC$_6$H$_4$)}Mg^{i}Pr [5] as an MMA polymerisation initiator

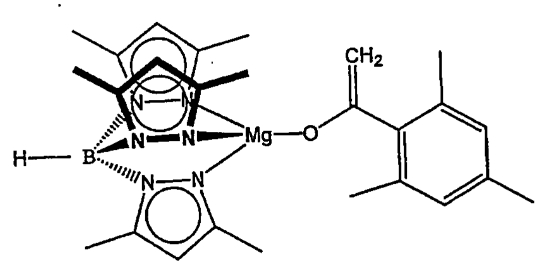
In toluene at -30°C, 200 equivalents MMA attains a conversion of 74% after 120 seconds.

M_n = 24,677 (M_n calc = 14,800), M_w/M_n = 1.20

Syndiotactic content (% rr triad) = 85%

Example 14

Synthesis of {HB(3,5-Me$_2$C$_3$N$_2$H)$_3$}Mg(OC(=CH$_2$)-2,4,6-Me$_3$C$_6$H$_2$) [6]



Potassium tris(3,5-dimethylpyrazolyl)borate (0.8945g, 2.66 x 10^{-3}mol) was suspended in 20cm^3 THF. 1.36cm^3 ^{i}PrMgCl (2.0M in Et$_2$O, 2.72 x 10^{-3}mol, 1.02 equivalents) was added via syringe at room temperature and the resultant white suspension was stirred for 6 hrs at 60°C. The reaction mixture was then allowed to cool to room temperature before a 10cm^3 THF solution of 0.4401g 2',4',6'-trimethylacetophenone (2.71 x 10^{-3}mol, 1.02 equivalents) was added dropwise over 2 minutes. The reaction was stirred at room temperature for 16 hours, filtered and concentrated to a white solid. This was washed with 5 cm^3 cold pentane (-78°C) and dried in vacuo to afford a free flowing white powder.

^{1}H NMR ($CDCl_3$): δ 6.83 (s, 2H, 2,4,6-$Me_3C_6H_2$), 4.19 (d, $^2J_{HH}$ = 0.8Hz, 1H, OC(=C*H*H)Ar'), 3.70 (d, $^2J_{HH}$ = 0.9Hz, 1H, OC(=CH*H*)Ar'), 3.70 (s, br, B*H*), 2.47 (s, 6H, mesityl *o-CH₃*), 2.35 (s, 9H, HB{$C_3N_2H(CH_3)_2$}), 2.26 (s, 3H, mesityl *p*-CH_3), 2.22 (s, 9H, HB{$C_3N_2H(CH_3)_2$})

Example 15

Use of {HB(3,5-$Me_2C_3N_2H)_3$}Mg(OC(=CH_2)-2,4,6-$Me_3C_6H_2$) [6] as an MMA polymerisation initiator

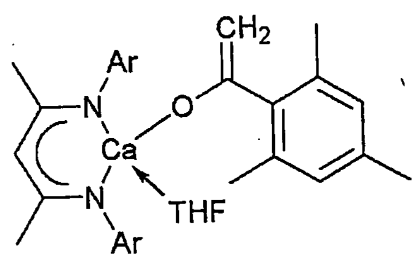
0.0080g {HB(3,5-$Me_2C_3N_2H)_3$}Mg(OC(=CH_2)-2,4,6-$Me_3C_6H_2$) (1.66 x 10^{-5}mol) was dissolved in 2 cm^3 toluene and chilled to -30°C. To this solution was added a 1 cm^3 toluene solution of MMA (0.3360g, 3.36 x 10^{-3}mol, 202 equivalents) and the reaction was stirred for 2 hours at -30°C.

M_n = 31,100 (calc = 20,200), M_w/M_n = 1.52

Triad analysis (by ^{1}H NMR): 14.5% mm : 20.5% rm : 65.0% rr

Example 16

Synthesis of {HC(C(Me)=N-2,6-$^iPr_2C_6H_3)_2$}Ca(OC(=CH_2)-2,4,6-$Me_3C_6H_2$)•THF [7]



Ar = 2,6-$^iPr_2C_6H_3$

{HC(C(Me)=N-2,6-$^iPr_2C_6H_3)_2$}CaNTMS$_2$•THF (0.0089g, 1.29 x 10^{-5}mol) and 2',4',6'-trimethylacetophenone (0.0021g, 1.29 x 10^{-5}mol) were mixed together in THF-d_8. ^{1}H NMR spectroscopy confirms the formation of {HC(C(Me)=N-2,6-$^iPr_2C_6H_3)_2$}Ca(OC(=CH_2)-2,4,6-$Me_3C_6H_2$) •THF and HNTMS$_2$.

^1H NMR (THF-d_8): δ 7.06 (m, br, 6H, N-2,6-$^iPr_2C_6H_3$), 6.60 (s, br, 2H, 2,4,6-Me-$_3C_6H_2$), 4.85 (s, br, 1H, $HC\{C(^tBu)$=NAr$\}_2$), 4.73 (s, br, 1H, OC(=C*H*H)Ar'), 3.41 (s, br, 1H, OC(=CH*H*)Ar'), 3.17 (m, br, 4H, C*H*MeMe), 2.16 (s, br, 6H, mesityl *o-CH₃*), 1.70 (s, br, 6H, HC{C(C*Me*)=NAr}$_2$), 1.60 (s, 3H, mesityl *p*-CH_3), 1.11 (m, br, 24H, $^3J_{HH}$ = 6.8Hz, CH*Me*$_2$).

Example 17

Synthesis of [{HC(C(Me)=N-2,6-$^iPr_2C_6H_3)_2$}Ca(OC(=CH_2)-2,4,6-$Me_3C_6H_2$)]$_n$ **[8]**

Mixing {HC(C(Me)=N-2,6-$^iPr_2C_6H_3)_2$}CaNTMS$_2$•THF (0.0219g, 3.17 x 10^{-5}mol) and 2',4',6'-trimethylacetophenone (0.0051g, 3.17 x 10^{-5}mol) in benzene-d_6 affords [{HC(C(Me)=N-2,6-$^iPr_2C_6H_3)_2$}Ca(OC(=CH_2)-2,4,6-$Me_3C_6H_2$)]$_n$.

^1H NMR (C_6D_6):δ 7.19-7.06 (m, 6H, N-2,6-$^iPr_2C_6H_3$), 6.65 (s, 2H, 2,4,6-$Me_3C_6H_2$), 4.62 (s, 1H, $HC\{C(^tBu)$=NAr$\}_2$), 4.18 (s, br, 1H, OC(=C*H*H)Ar'), 3.83 (s, br, 1H, OC(=C*H*H)Ar'), 3.12, 3.04 (sept, 4H, $^3J_{HH}$ = 6.9Hz, C*H*MeMe), 2.10 (s, 6H, mesityl *o*-CH_3), 1.98 (s, 3H, mesityl *p*-CH_3), 1.53 (s, 6H, HC{C(*Me*)=NAr}$_2$), 1.16 - 1.08 (m, br, 24H, CH*Me*Me)

Example 18

Use of [{HC(C(Me)=N-2,6-$^iPr_2C_6H_3)_2$}Ca(OC(=CH_2)-2,4,6-$Me_3C_6H_2$)]$_n$ **[8]** as an MMA polymerisation initiator

At -30°C a 0.5cm^3 toluene solution of 2',4',6'-trimethylacetophenone (0.0022g, 1.36 x 10^{-5}mol) was added to a 2cm^3 toluene solution of {HC(C(Me)=N-2,6-$^iPr_2C_6H_3)_2$}CaNTMS$_2$•THF (0.0091g, 1.32 x 10^{-5}mol). After stirring for 1 minute, MMA (0.2657g, 2.65 x 10^{-3}mol, 201 equivalents in 1cm^3 toluene) was added dropwise over 20s.

The polymerisation was stirred at -30°C for 5 minutes, then terminated with MeOH (25μl).

^1H NMR confirms that the PMMA is isotactic-biased: triad contents = 70.8% mm : 22.7% mr : 6.5% rr

M_n = 41,850, M_w/M_n = 6.09

Example 19

Synthesis of $\{HC(C(CH_3)=N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}MgNPr^i_2$ [9]

A stirred toluene solution of 2.0 x 10^{-3}mol [(BDI)$Mg^{n/s}Bu$] (formed in situ from the reaction of Bu_2Mg with $H_2C(C(CH_3)=N\text{-}2,6\text{-}^iPr_2C_6H_3)_2$) was cooled to -30°C and treated dropwise with $^iPr_2NH$ (290 μl, 2.1 x 10^{-3}mol). The resulting solution was allowed to warm to ambient temperature, and then stirred at 60 °C for 15 minutes. Volatiles were then removed in vacuo and the residue then extracted into pentane (35 ml). Upon standing at -30°C 0.67g crystals formed (62%).

^1H NMR (C_6D_6): δ 7.12 (m, 6H, *m-H, p-H*), 4.84 (s, 1H, $HC\{C(CH_3)NAr\}_2$), 3.23 (sept, 4H, $^3J_{HH}$ = 6.7Hz, $CHMe_2$), 3.07 (sept, 2H, $^3J_{HH}$ = 6.1Hz, $NCH(CH_3)_2$), 1.66 (s, 6H, $HC\{C(CH_3)NAr\}_2$), 1.34 (d, 12H, $^3J_{HH}$ = 6.9Hz, $CH(CH_3)_2$), 1.17 (d, 12H, $^3J_{HH}$ = 6.9Hz, $CH(CH_3)_2$), 0.87 (d, 12H, $^3J_{HH}$ = 6.1Hz, $NCH(CH_3)_2$).

Example 20

Use of $\{HC(C(CH_3)=N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}MgNPr^i_2$ [9] as an MMA polymerisation initiator

In toluene at -30°C, 200 equivalents MMA were mixed with $\{HC(C(CH_3)=N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}MgNPr^i_2$. The polymerisation was terminated after 90seconds with MeOH. A conversion of 94% was measured by ^1H NMR spectroscopy.

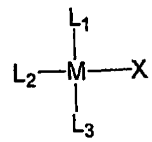
M_n = 19,550 (M_n calc = 18,800); M_w/M_n = 1.05.

Syndiotactic content (% rr triad) >90%

Various modifications and variations of the described methods of the invention will be apparent to those skilled in the art without departing from the scope and spirit of the invention. Although the invention has been described in connection with specific preferred embodiments, various modifications of the described modes for carrying out the invention which are obvious to those skilled in chemistry or related fields are intended to be within the scope of the following claims.

CLAIMS

1. A complex of formula I



I

wherein

M is Ca, Mg, Ba or Sr;

L_1 is selected from R^1O, R^2S, R^3R^4N, R^5R^6P, a substituted or unsubstituted cyclopentadienide and a substituted or unsubstituted pyrazolyl group, where R^{1-6} are each independently H or hydrocarbyl;

L_2 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7R^8C{=}NR^9$, $PR^7R^8R^9$, or a substituted or unsubstituted heterocycle containing one or more O, N or S atoms, where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand;

L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2, wherein L_3 may be the same or different to L_2; or L_3 is linked to a further metal centre; or L_1, L_2 and L_3 are linked to form a tridentate ligand; and

X is an alkyl group, an aryl group, an amide group, an aryloxide or an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, wherein R^{10-12} are each independently H or hydrocarbyl;

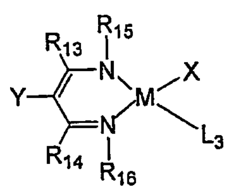
with the proviso that when L_1 and L_2 are $\{HC(C(CH_3){=}N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}$ and M is magnesium, X is other than Me or ${}^tBu$.

2. A complex according to claim 1 wherein R^1 and R^2 are hydrocarbyl, and R^{3-6} are H or hydrocarbyl.

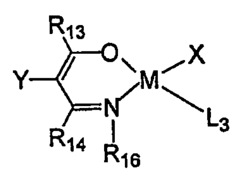
3. A complex according to claim 1 wherein R^1 and R^2 are each independently selected from branched or unbranched alkyl, branched or unbranched alkenyl, or aryl, each of which may be substituted or unsubstituted.

4. A complex according to claim 1 wherein L_1 and L_2 are linked to form a bidentate ligand selected from a beta-diketiminate and a beta-ketoiminate.

5. A complex according to claim 4 of formula II or III



II



III

wherein

Y is H, hydrocarbyl or CN;

R^{13-16} are each independently selected from H and hydrocarbyl; or Y and R^{13} are linked to form a hydrocarbyl group; and

L_3 absent or as defined in claim 1.

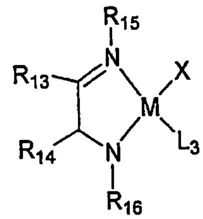
6. A complex according to claim 5 wherein

Y is selected from H, CN, alkyl, aryl, haloalkyl or heteroalkyl;

R^{13-16} are each independently selected from alkyl, aryl, heteroalkyl, haloalkyl, cycloalkyl and a heterocyclic ring containing at least one O, N or S atom; or Y and R^{13} are linked to form an aryl group; and

L_3 is absent or is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7C{=}NR^8$, $PR^7R^8R^9$, thiophene and tetrahydrofuran, where R^{7-9} are each independently H or a hydrocarbyl group.

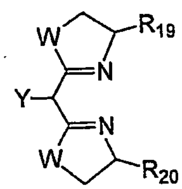
7. A complex according to claim 1 of formula V



V

wherein R^{13-16} are as defined in claim 5 or claim 6, and where R^{13} and R^{15} are optionally linked to form an aryl group.

8. A complex according to claim 1 wherein L_1 and L_2 form a bidentate ligand of formula VIII



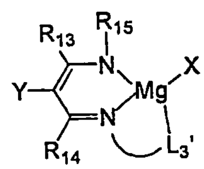
VIII

wherein
Y is as defined above;
W is O, NH, NR' or CH_2 where R' is hydrocarbyl; and
R^{19-20} are as defined for R^{13-16} above.

9. A complex according to any one of claims 1 to 3 wherein L_1, L_2 and L_3 are linked to form a tridentate ligand.

10. A complex according to claim 9 wherein L_1, L_2 and L_3 are linked to form a tridentate ligand selected from a beta-diketiminate with a pendant donor group, and a Schiff base derivative with a pendant donor arm.

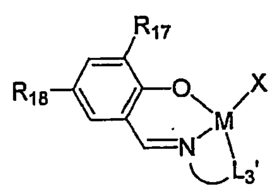
11. A complex according to claim 10 of formula VI



VI

wherein L_3' is defined as for L_3 in claim 1, and is linked to the nitrogen of the bidentate ligand via a linker group.

12. A complex according to claim 10 wherein said complex is of formula VII

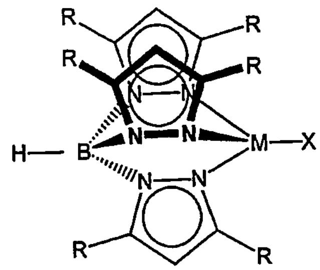


VII

wherein L_3' is defined as for L_3 in claim 1, and is linked to the nitrogen of the bidentate ligand via a linker group, and R^{17-18} are as defined for R^{13-16} above .

13. A complex according to claim 11 or claim 12 wherein the linker group is $(CH_2)_n$ where n is 0-6, an arylene group, or SiR_2, where R is hydrocarbyl.

14. A complex according to claim 1 of formula X



X

wherein each R is independently H or a hydrocarbyl group.

15. A compound according to any preceding claim wherein X is an alkyl group

16. A compound according to claim 15 wherein X is ^{i}Pr.

17. A compound according to any one of claims 1 to 14 wherein X is an amide group.

18. A compound according to claim 17 wherein X is NPr^{i}_{2}.

19. A compound according to any one of claims 1 to 14 wherein X is an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, wherein R^{10} and R^{11} are H and R^{12} is an aryl group.

20. A compound according to claim 19 wherein X is -OC (=CH_2)Ar, wherein Ar is 2,4,6,-$Me_3C_6H_2$.

21. A complex comprising a dimer of a complex according to any preceding claim.

22. A complex according to claim 1 selected from the following:
{$HC(C(CH_3){=}N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)_2$}$Mg^{i}Pr$ [1];
[{$HC(C(CH_3){=}N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)_2$}$Mg(OC({=}CH_2)Ar)$]$_2$ [2];
[{$HC(C(CH_3){=}N\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)_2$}Mg(OC(=CH2)Ar)•$Et_2O$] [3];

wherein Ar = 2,4,6,-$Me_3C_6H_2$;

$\{HC(C(^tBu)=N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}Mg(OC(=CH_2)\text{-}2,4,6\text{-}Me_3C_6H_2)$ **[4]**;

$\{HC(C(Me)=N\text{-}2,6\text{-}^iPr_2C_6H_3)(C(Me)=N\text{-}2\text{-}OMeC_6H_4)\}Mg^iPr$ **[5]**;

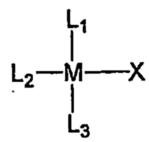
$\{HB(3,5\text{-}Me_2C_3N_2H)_3\}Mg(OC(=CH_2)\text{-}2,4,6\text{-}Me_3C_6H_2)$ **[6]**;

$\{HC(C(Me)=N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}Ca(OC(=CH_2)\text{-}2,4,6\text{-}Me_3C_6H_2)\cdot THF$ **[7]**;

$[\{HC(C(Me)=N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}Ca(OC(=CH_2)\text{-}2,4,6\text{-}Me_3C_6H_2)]_n$ **[8]** where n = 1 or 2; and

$\{HC(C(CH_3)=N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}MgNPr^i_2$ **[9]**.

23. Use of a complex of formula Ia as a polymerisation initiator,



Ia

wherein

M is Ca, Mg, Ba or Sr;

L_1 is selected from R^1O, R^2S, R^3R^4N, R^5R^6P, a substituted or unsubstituted cyclopentadienide, and a substituted or unsubstituted pyrazolyl group, where R^{1-6} are each independently H or hydrocarbyl;

L_2 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7R^8C=NR^9$, $PR^7R^8R^9$, and a substituted or unsubstituted heterocycle containing one or more O, N or S atoms, where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand;

L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2, wherein L_3 may be the same or different to L_2; or L_3 is linked to a further metal centre; or L_1, L_2 and L_3 are linked to form a tridentate ligand; and

X is an alkyl group, an aryl group, an amide group, or an enolate group of formula $R^{10}R^{11}C=CR^{12}O$-, wherein R^{10-12} are each independently H or hydrocarbyl;

with the proviso that when L_1 and L_2 are $\{HC(C(CH_3)=N\text{-}2,6\text{-}{}^iPr_2C_6H_3)_2\}$, M is magnesium, X is other than Me or ${}^tBu$.

24. Use according to claim 23 in the polymerisation of acrylate and/or alkyl acrylate monomers.

25. Use according to claim 23 or 24 which further comprises the use of a chain transfer reagent.

26. A process for the polymerisation of acrylate and/or alkylacrylate monomers, said process comprising contacting an initiating amount of a complex of formula Ia as defined in claim 23 with an acrylate and/or an alkylacrylate monomer in the presence of a suitable solvent.

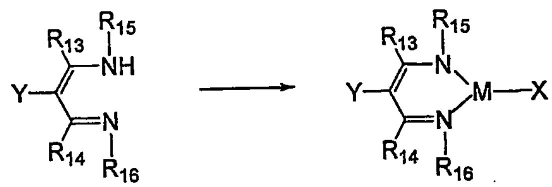
27. A process according to claim 26 wherein the ratio of monomer to the complex is between 10:1 and 10^6:1.

28. An article prepared by a process according to claims 26 or 27.

29. A composition comprising an acrylate and/or an alkylacrylate monomer and a complex of formula Ia as defined in claim 23.

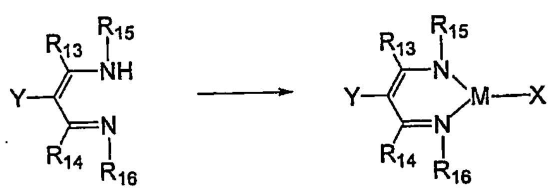
30. A composition comprising poly(alkylacrylate) and poly(alkylmethacrylate) or copolymers thereof, and a complex of formula Ia as defined in claim 23.

31. A process for preparing a complex of formula II as defined in claim 5, where X is alkyl, said process comprising reacting a compound of formula IX with (a) ^{n}BuLi, and (b) XMgCl



IX II

32. A process for preparing a complex of formula II as defined in claim 5, where X is alkyl, said process comprising reacting a compound of formula IX with MgX_2

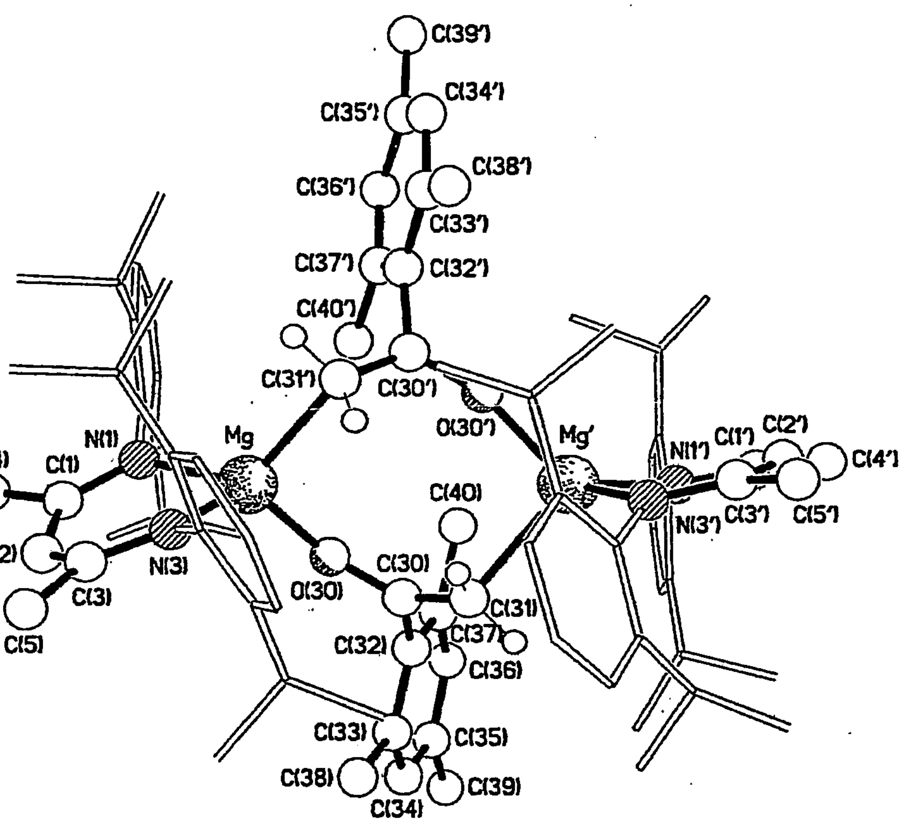


IX II

33. A process for preparing a complex of formula II, as defined in claim 5, where X is an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, said process comprising reacting the product obtained from the process of claim 31 or claim 32 with a compound of formula $HR^{10}R^{11}C\text{-}C(O)R^{12}$.

34. A method for producing polymethacrylate having greater than 75% syndiotacticity, said method comprising contacting methacrylate monomer with a complex of formula Ia as defined in claim 23 in the presence of a suitable solvent.

35. A method according to claim 34 which is carried out at a temperature in excess of -40°C.


C(39')
C(35')
C(34')
C(38')
C(36')
C(33')
C(37')
C(32')
C(40')
C(31')
C(30')
O(30')
Mg
Mg'
N(1)
N(1')
C(1')
C(2')
C(4')
C(4)
C(1)
C(3')
C(5')
N(3')
C(40)
C(2)
C(3)
N(3)
O(30)
C(30)
C(31)
C(5)
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C(37)
C(36)
C(33)
C(35)
C(38)
C(34)
C(39)

FIGURE 1

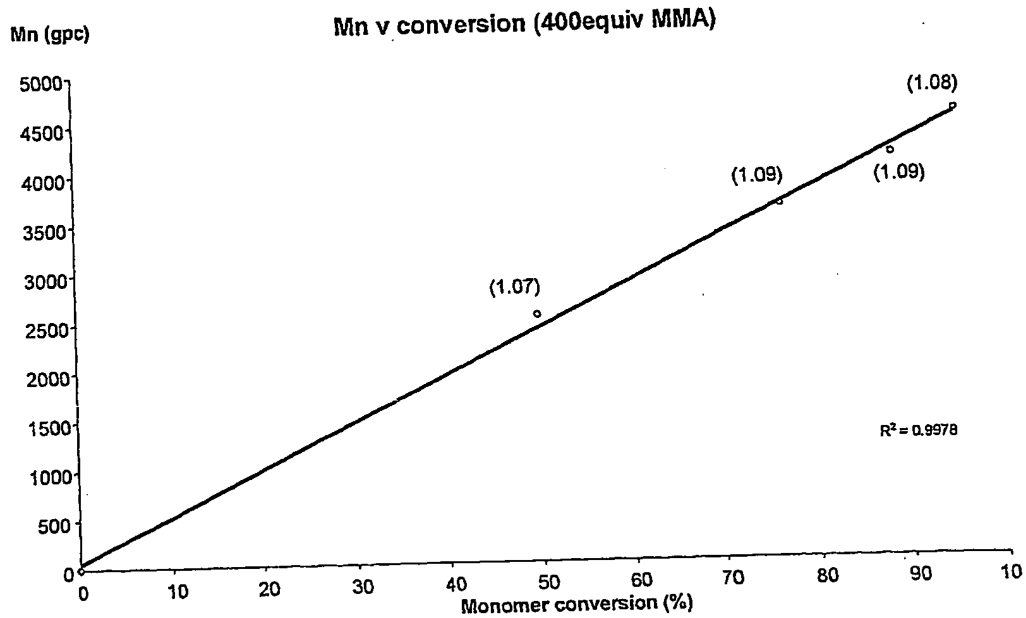
Mn v conversion (400equiv MMA)
Mn (gpc)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
60
70
80
90
10
Monomer conversion (%)
(1.08)
(1.09)
(1.09)
(1.07)
$R^2 = 0.9978$

FIGURE 2

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(81) **Designated States** (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

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Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv)) for US only*

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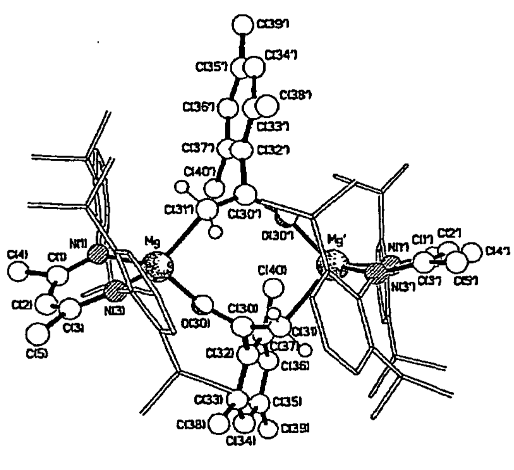
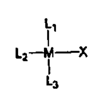
— *with international search report*

[Continued on next page]

(54) **Title:** COORDINATION COMPLEX





(I)

(57) **Abstract:** The present invention provides a complex of formula (I) wherein M is Ca, Mg, Ba or Sr; L_1 is selected from R^1O, R^2S, R^3R^4N, R^5R^6P, a substituted or unsubstituted cyclopentadienide, and a substituted or unsubstituted pyrazolyl group, where R^{1-6} are each independently H or hydrocarbyl; L_2 is selected from R^7R^8O, R^7R^8S, $R^7R^8R^9N$, $R^7R^8C{=}NR^9$, $PR^7R^8R^9$, and a substituted or unsubstituted heterocycle containing one or more O, N or S atoms, Where R^{7-9} are each independently H or a hydrocarbyl group; or L_1 and L_2 are linked to form a bidentate ligand; L_3 is absent or is a solvent molecule, or a neutral ligand as defined for L_2, wherein L_3may be the same or different to L_2; or L_3 is linked to a further metal center ; or L_1, L_2 and L_3 are linked to form a tridentate ligand; and X is an alkyl group , an aryl group, an aryloxide, an amide group, or an enolate group of formula $R^{10}R^{11}C{=}CR^{12}O$-, wherein R^{10-12} are each independently H or hydrocarbyl; with the proviso that when L_1 and L_2 are $\{HC(C(CH_3){=}N\text{-}2,6\text{-}^iPr_2C_6H_3)_2\}$ and M is magnesium , X is other than Me or ^tBu.

WO 03/062249 A3

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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27 November 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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International Application No
PCT/GB 03/00163

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07F3/00 C07F3/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GIBSON, VERNON C. ET AL: "Novel Mono-alkyl Magnesium Complexes Stabilized by a Bulky.beta.-Diketiminate Ligand: Structural Characterization of a Coordinatively Unsaturated Trigonal System" JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (2000), 122(29), 7120-7121, XP002234846 Scheme 1: compounds 2-4 page 7120, column 2; figures 1-3	1-6,15, 21
X	page 7121, column 2, paragraph 3	23,24,26
X	page 7121, column 1	32
X	EP 0 747 405 A (BRIDGESTONE CORPORATION, JAPAN) 11 December 1996 (1996-12-11) page 5, line 35 - line 55	1,2
X	page 11, line 1 -page 16	23

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
25 September 2003	01 10. 2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Richter, H

INTERNATIONAL SEARCH REPORT

Intern. Application No
PCT/GB 03/00163

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WEEBER, ARMIN ET AL: "Homoleptic and Heteroleptic Barium Benzyl Complexes: Synthesis and Reactivity as Initiators for Anionic Styrene Polymerizations" ORGANOMETALLICS (2000), 19(7), 1325-1332, XP000920607	1-3
X	compound 6: (C5Me5)2Ba.2THF; page 1327, column 2 barium bis(2,4,6-tri-tert.-butyl phenolate.2THF page 1330, column 2, line 32 - line 33 ---	1-3
X	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; RAMIREZ, FAUSTO ET AL: "Preparative chemistry of organic magnesium oxyanion complexes. 5. Aroxide complexes" retrieved from STN Database accession no. 91:32007 XP002234848 abstract; figures 21,22 & SYNTHESIS (1979), (1), 71-4, ---	1-3
X	DATABASE CROSSFIRE BEILSTEIN [Online] Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Tetrahedron, 53; 22; 7671-7688, 1997 DESIMONI, G. ET AL.: Database accession no. BRN 7792064 XP002234867 abstract ---	1-4,8
A	ZHONG, ZHIYUAN ET AL: "A Novel and Versatile Calcium-Based Initiator System for the Ring-Opening Polymerization of Cyclic Esters" MACROMOLECULES (2001), 34(12), 3863-3868, XP002234847 Ca[NSiMe3)2]2(THF)2 page 38633 -page 3867; table 1 ---	1-3,17, 23
A	XVIIth International Conference on Organometallic Chemistry; Munich, August 16-21, 1998, Part 1 Poster Session A; D.Schramm, W.Kläui "Synthesis of Cationic Hydrotris(pyrazolyl)borate Zirconium Compounds" XP002249590 A 150 abstract -----	9,14

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 03/00163

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 4-8,31-33; partially: 1-3,15-30,34,35

   Bidentate complexes falling within formula I according to claim 1, their preparation and use

1.1. Claims: partially 1-3,15-30,34,35
   Monodentate complexes of formula I and their use

2. Claims: 9-14, partially 1-3,15-30,34,35

   Tridentate complexes falling within formula I according to claim 1 and their use

Please note that all inventions mentioned under item 1,-although not necessarily linked by a common inventive concept, could be searched without effort justifying an additional fee.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/00163

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0747405	A	11-12-1996	US	5610227	A	11-03-1997
			CA	2178145	A1	08-12-1996
			DE	69601327	D1	25-02-1999
			DE	69601327	T2	27-05-1999
			EP	0747405	A1	11-12-1996
			ES	2126353	T3	16-03-1999
			JP	9003111	A	07-01-1997